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Production of $PbTiO_3$ nanoparticles for inkjet printing: a comparison of solid state and molten salt processing conditions

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Introduction

The incorporation of piezoelectric materials to the inkjet printing process has the potential to allow full device integration, for example, of pressure sensors, energy harvesting and energy storage capacitors. The problem with approaches to date in this area are that the functional properties of in-device materials are under-developed due to incomplete thermal processing into ceramics and hence are ill-defined in terms of morphology, crystallographic orientation and electrical properties. The challenge is therefore to produce high quality ferroelectric crystals, where the upper size is set by current ink-jet printing technology.

Here we compare lead titanate (PT) nanocrystals produced by two different processing routes: low temperature calcination (LTC) and molten salt processing (MSP). Variation in processing conditions (e.g. temperature, salt ratio) and size of titanium dioxide starting materials have been investigated.

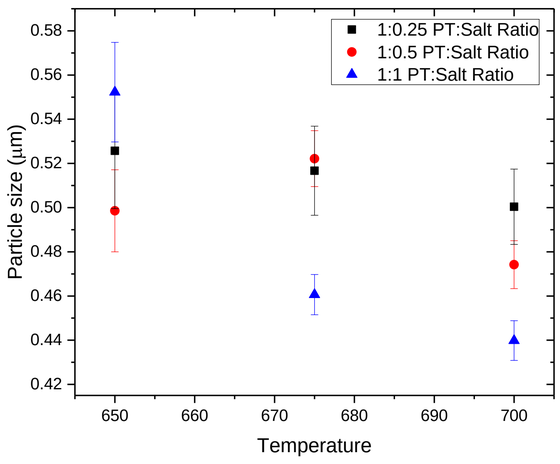
Molten Salts Processing (MSP)

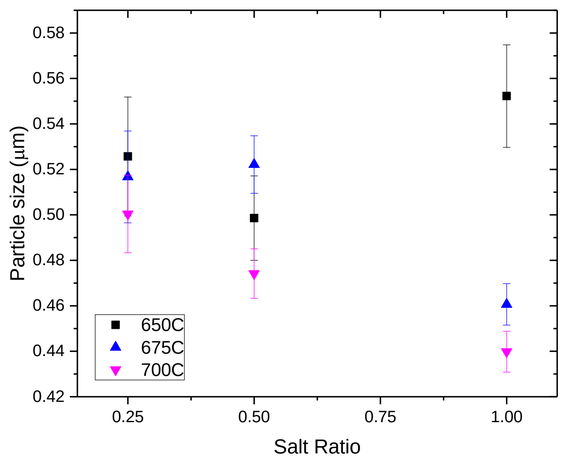
PT samples were produced by a mixed oxide synthesis route consisting of drying lead oxide and titanium dioxide powders in an oven, weighing a stoichiometric ratio then adding 2-propanol and zirconium beads and ball-milling for 24 hours, then evaporating the 2-propanol (and extracting the Zr beads) with stirring followed by oven drying. The mix was then sieved through a 300 μm nylon mesh. Two different titanium dioxides were used: one with micrometre sized particles and one with nanoscale sized.

The samples were then mixed in a potassium chloride/sodium chloride eutectic salt mix and calcined at a range of temperatures from 600 to 850°C. For some samples, lithium chloride or lithium fluoride were added to the salt mix. After calcining, the PT was recovered by dissolving the salt flux in water, with regular water changes until no chloride ions were detected by silver nitrate solution and then left to dry.

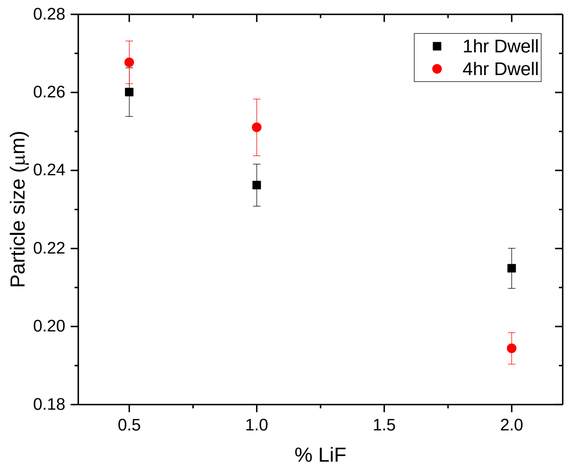
Particle size analysis was achieved by observing the PT samples with scanning electron microscopy (SEM) followed by image analysis. The size of the discrete X-ray scattering volume (grain size) was determined by Williamson-Hall analysis of wide angle X-ray diffraction (XRD) patterns of the PT powders.

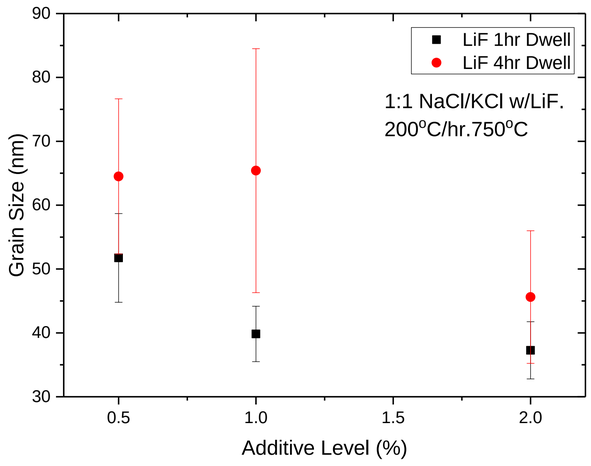
Micrometre sized TiO_2





PT particle size was seen to decrease with increasing calcination temperature (L) and with increasing salt ratio (R), although changes were relatively small.

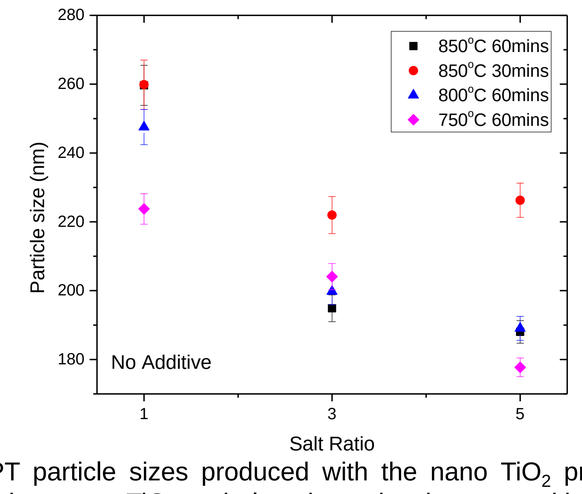


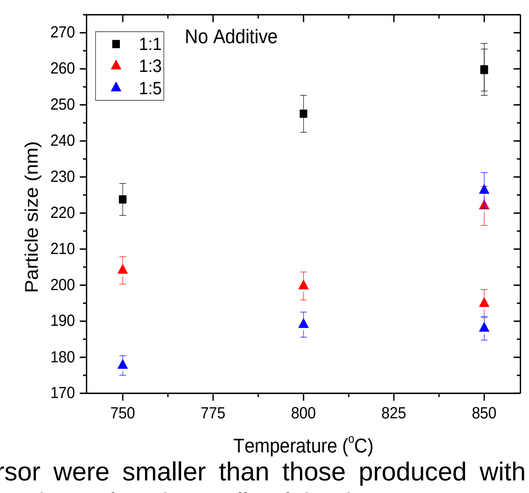


When a lithium fluoride additive was added, the PT particle size decreased to 260 nm (no additive 440 nm), and was seen to decrease further to 190 nm as the amount of additive increased. A similar trend was seen for the lithium chloride additive.

All PT particles sizes were an order of magnitude greater than XRD grain size (~50-60 nm) for all MSP samples produced. There was a small decrease in grain size with additive level.

Nano sized TiO_2





PT particle sizes produced with the nano TiO_2 precursor were smaller than those produced with the micrometre TiO_2 and also showed a decrease with increasing salt ratio at all calcination temperatures. A different trend was seen with temperature, where PT particle size increased with calcination temperature.

Grain size was similar (~50-60 nm) to that with the micrometre TiO_2, showing similar processing trends.

Conclusions

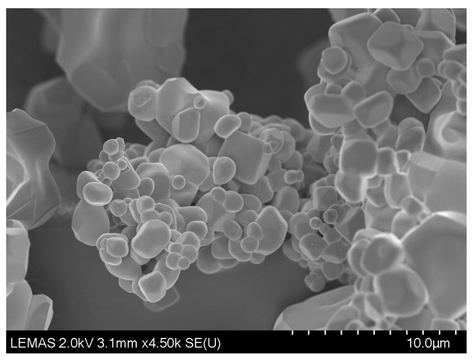
- PT particle size in MSP was seen to decrease with increasing flux ratio.
- PT grain size in MSP was observed to be an order of magnitude less than particle size.
- The addition of Lithium salt additive to the salt flux resulted in a decrease in particle size.
- The use of a nano TiO_2 precursor resulted in smaller particles from MSP.

- LTC produced larger, less agglomerated particles.
- PT was produced at a lowest calcination temperature of 600°C
- Hot stage XRD is being used to investigate the differences between LTC and MSP.

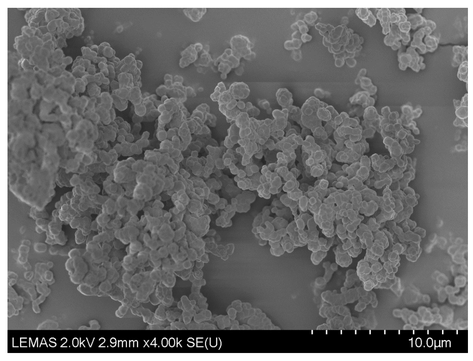
Low Temperature Calcination (LTC)

PT samples were produced by following the same mixed oxide synthesis route as MSP until the calcination step. LTC samples were prepared without salt flux and calcined in atmosphere at temperatures from 450 to 650°C. As with the MSP, both a nanoscale TiO_2 and a micrometre TiO_2 were used.

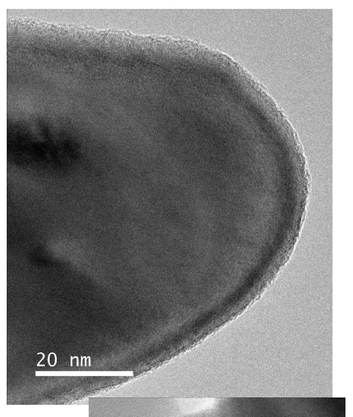
Samples were observed under SEM, transmission electron microscopy (TEM) and XRD.

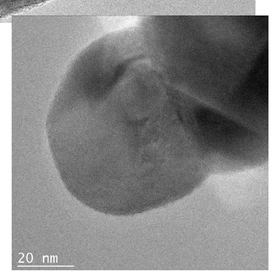


SEM: Nano TiO_2 derived PT calcined at 600°C



SEM: Micrometre TiO_2 derived PT calcined at 600°C





TEM: Nano TiO_2 derived PT calcined at 600°C.

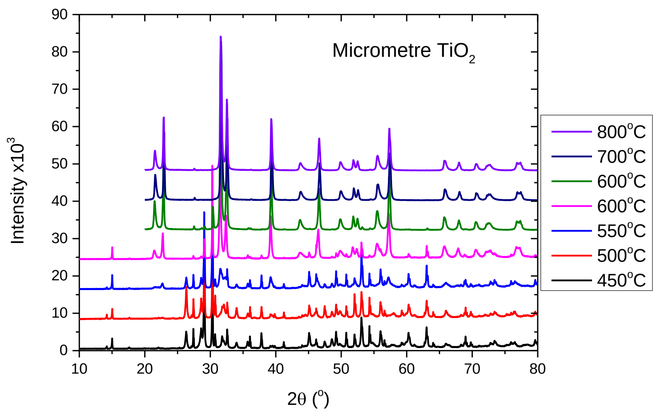
Calcination at 'low' temperatures produced larger PT particles than the MSP process, that were, in general, less agglomerated. These particles could be broken up by a mechanical attrition process.

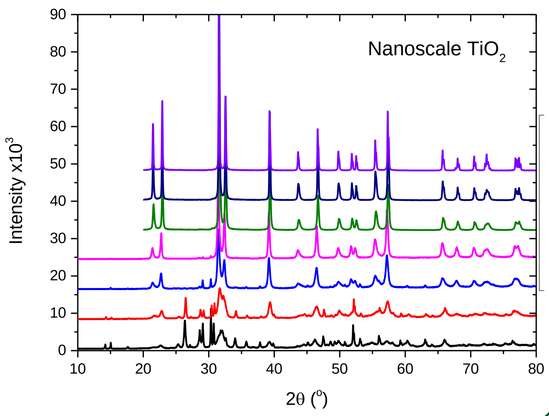
The PT particles produced by the MSP process show clear 'necking' between each other, whereas the particles from LTC are more isolated, particularly with the nano TiO_2

TEM showed that the PT particles formed by LTC using the nano TiO_2 were close to being single crystals, with few grain boundaries.

XRD of samples produced at different calcination temperatures showed that the lowest temperature at which PT could be formed was 600°C using the nano TiO_2 and 700°C for the micrometre sized TiO_2.

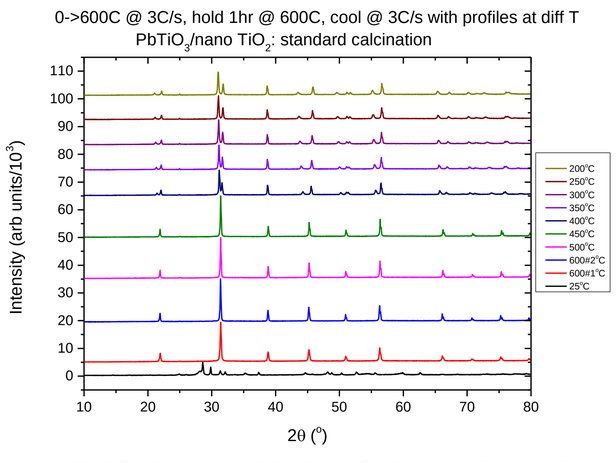
XRD patterns at different calcination temperatures.
L: μm TiO_2 R: nm TiO_2

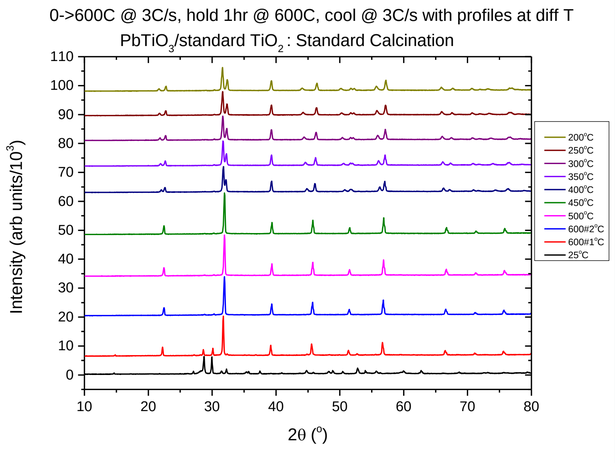


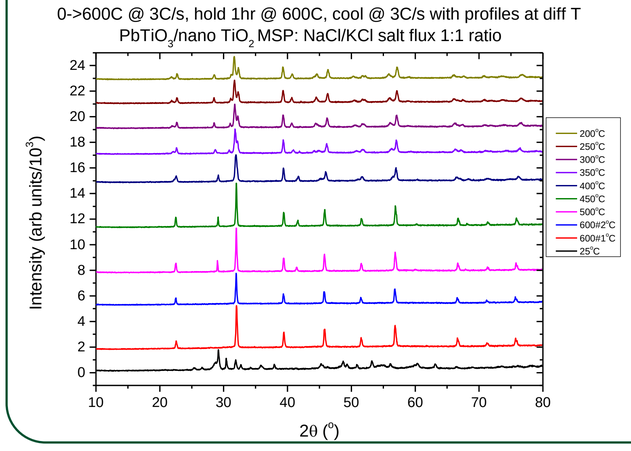


Hot Stage XRD comparison of MSP and LTC

Hot stage XRD was used to calcine a series of samples whilst simultaneously performing XRD acquisitions. Both MSP and LTC samples were prepared in this fashion. The powders were prepared by the same route as those prepared for standard LTC and MSP.







MSP and LTC were compared using hot stage XRD.

This work is still ongoing, but data to date confirms the results from samples produced in the furnace.

The nano TiO_2 samples show that a good quality PT is formed at 600°C, but with the micrometre TiO_2, the PT is not formed until higher temperatures.